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VOLUME XXVIII NOVEMBER, 1911 NO. 3.

PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS CONTAINING AMMONIA AND CITRIC ACID.*

BY ROBERT A. HALL AND JAMES M. BELL.

In the analysis of commercial fertilizers for the so-called "available" phosphoric acid, it is usual to employ a solution of "exactly neutral" ammonium citrate,[1] having a specific gravity of 1.09 at 20°. After extraction of the fertilizer with water, the residue is treated with the citrate solution and the phosphoric acid which remains undissolved is termed insoluble, or non-available; that which the water dissolves is the water-soluble; and that dissolved in the citrate solution is the reverted or citrate-soluble. The sum of the water-soluble and the citrate-soluble phosphoric acid constitutes the available. Upon the results of these analyses depend the valuation of the fertilizer material, and, if the guarantee accompanying the fertilizer claims a higher percentage of phosphoric acid than is shown in the analysis by the state chemist, the manufacturer is liable to a fine.

In the preparation of the "exactly neutral" ammonium citrate solution, however, great difficulty is encountered, due to the lack of sensitiveness of every color indicator. This lack of sensitiveness in the color indicator is general in the neutralization of a weak base, such as ammonium hydroxide, by a weak acid, such as citric acid.

The Association of Official Agricultural Chemists prescribes[1] the use of a saturated alcoholic solution of corallin as indicator in testing for the neutrality of the citrate solution; also an "optional

*Reprinted from The Journal of the American Chemical Society, Vol. XXXIII, No. 5. May, 1911.

[1]Bureau of Chemistry, *Bull.* 107 (revised), 1.

method'' wherein the citrate is precipitated by an alcoholic solution of calcium chloride, and the filtrate tested for acidity or alkalinity with cochineal as indicator. This method is employed apparently with the object of avoiding the difficulty experienced in determining the end point in the former method. That both methods are unreliable and unsatisfactory is evidenced by the fact that at almost every meeting of chemists engaged in fertilizer analyses there is animated discussion of, and general protest against both the ''official method'' and the ''optional method'' on account of the difficulty in getting a sharp end point with corallin, or any other color indicator.

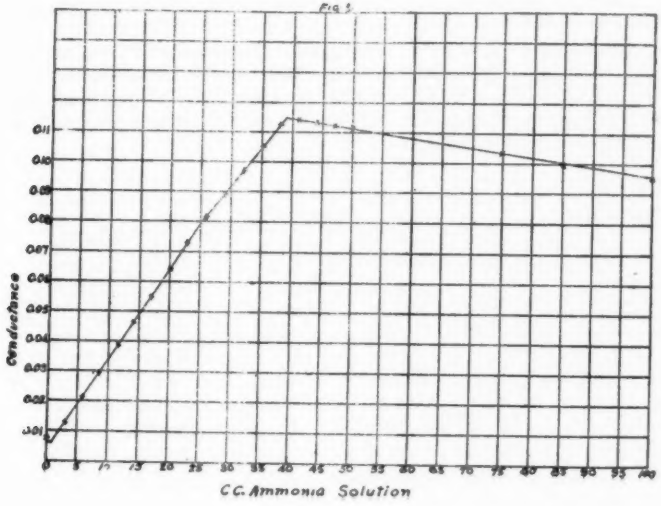
In the absence of any satisfactory color indicator of the end point in the neutralization of a weak acid by a weak base, several physical properties of mixtures of ammonia and citric acid have been investigated with a view of applying these to the determination of the end point. The use of conductivity as an indicator of neutrality has been demonstrated by Küster and Grüters[2] in the titration of weak acids by strong bases, the conductivity being measured after each addition of the base to the solution. By plotting the quantity of alkali against the conductivity, a decided break was found in the curve just at the neutral point. The solution consisted of a mixture of the acid and salt in varying proportions up to the neutral point, after which it was composed of the alkali and salt. The method of conductance has also been employed to determine the acidity of colored liquids,[3] such as wines, where the color of the liquid would mask the color change of the indicator.

Another physical measurement has been used by Ostwald, viz., density, as an indicator of the neutral point, a sharp break in the composition-density curve being found at this point of neutrality.

The present paper contains the results of measurements of conductivity and of density of a series of solutions containing constant amounts of citric acid and varying amounts of ammonia in a fixed volume of solution. The conductivity measurements were made

1. Bur. of Chem., *Bull.* 107 (revised), 1.
2. *Z. anorg. Chem.*, 35, 454 (1903).
3. Kuster and Gurters, *Loc. cit.*; Geibel, Z. *anorg. Chem.*, 42, 231 (1905).

with the usual Wheatstone apparatus, the conductivity cell used being of the H. C. Jones type, designed for concentrated solutions. In making up the solutions standardized (D. & R.) pipets, burets, and flasks were used, and also, as a check, the flask and contents were weighed after each addition This was deemed advizable on account of the very concentrated solutions used and on account of the volatility of the ammonia. In order to minimize the loss of ammonia by evaporation, the stock solution was siphoned from a bottle protected with a capillary opening. The flow of liquid into the buret was controlled by a glass stopcock, and the top of the buret was closed except for a capillary opening. The outflow from the buret was made through a small tube, drawn to a capillary opening, of sufficient length to pass nearly to the bottom of the flask in which the solutions were mixed. This capillary tube was coated on the outside with a high-melting paraffin to prevent the solution in the flask clinging to the tube when the ammonia solution was led into the body of the citric acid solution. The escape of ammonia was thus minimized or prevented entirely, no ammo-



nia being noticeable by odor or by a change of color of moist neutral litmus paper.

Each solution in the first series of conductivity measurements had a total volume of 200 cc. This contained 100 cc. of a solution of pure citric acid (Kahlbaum's), 370 grams per liter, thus approximating the citrate content of the solution employed in fertilizer analysis.[1] To these solutions were added in the way described above varying amounts of the ammonia solution, whose exact strength was determined both by titration against standardized acid aud also by density determinations. The 200 cc. measuring flask was then cooled and filled up to the mark with distilled water. After thorough mixing, the solutions were transferred to glass-stoppered bottles and placed in the thermostat which was electrically heated and controlled. The temperature was maintained at 25°, within 0.01°. This temperature was chosen rather than 20°, at which the fertilizer chemist makes this specific gravity determination, because of the inconveniences of running a thermostat at a temperature below that frequently existing in this neighborhood.

In another series of measurements the above solutions were diluted one-half, 100 cc. to 200 cc., and the conductivities ascertained.

In Table I are given the results of the conductivity measurements of the concentrated solutions, made as described above. The quantity of citric acid solution used was always 100 cc., weighing 113.00 ± 0.02 grams. In figure I the conductivities are plotted against the cc. of ammonia.

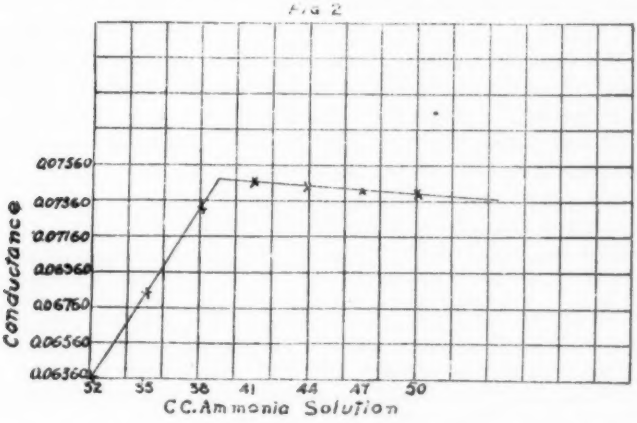
TABLE I.

Solution no.	Ammonia solution cc.	Conductivity	Solution no.	Ammonia solution cc.	Conductivity
1	0.00	0.007791	12	32.00	0.09731
2	3.00	0.01292	13	35.00	0.1052
3	5.75	0.02113	14	38.00	0.1124
4	8.60	0.02943	15	41.00	0.1145
5	11.55	0.03901	16	44.00	0.1132
6	14.31	0.04629	17	47.00	0.1124
7	17.15	0.05500	18	50.00	0.1116
8	20.00	0.06401	19	75.00	0.1032
9	23 00	0.07271	20	85.00	0.09990
10	26.00	0.08187	21	100.00	0.09523
11	29.00	0.08984			

1. *Loc cit.*

It will be seen in Figure I that there is a sharp break in the curve at the point representing 39 cc. of the ammonia solution. The strength of the ammonia solution used in these experiments was determined by density measurements and also by titration against hydrochloric acid of known strength. This acid was compared with a solution of caustic soda, which was standardized by comparison with a normal solution of oxalic acid made by weighing the exact amount of oxalic acid. The titrations with oxalic acid were made with phenolphthalein, and those with ammonia with methyl orange as indicator. . By this method the ammonia was found to be 13.51 normal. Therefore, the 39 cc of ammonia solution contains 0.5268 mols. NH_3. Of citric acid in 100 co. of acid solution there are 37 grams, equal to 0.156 mols. Now, $0.5268/0.176=2.993$; that is, the neutral solution, as determined by this method is at triammonium citrate.[1] This suggests the applicability of the conductivity method for determining the neutral point of ammonium citrate solution.

Some of the above solutions were diluted one-half; that is, 100 cc. of the solution were diluted to 200 cc , and the conductivities



ascertained. In Table II the measurements are given, and in Fig.

1. Van Itallie, *Z. anorg. Chem.*, 60, 358 (1908).

2 the conductivities are plotted against the cc of ammonia solution as before. The break in the conductivity curve of the diluted solutions agrees with that found for the more concentrated ones, showing that a dilution of one-half has no influence on the neutral point as found by this method.

TABLE II.

Solution no.	Ammonia solution cc.	Conductivity.	Solution no.	Ammonia solution cc.	Conductivity
12.....	32.00	0.06360	16	44.00	0.07440
13.....	35.00	0.06841	17.....	47.00	0.07418
14.....	38.00	0.07330	18.....	50,00	0.07402
15.....	41.00	0.07471			

It will be noticed further in the curve of Fig. I that the first point of the curve does not fall in the smooth curve with the other points up to the neutral point. To investigate the failure of this point to fall on the regular curve there was made a further series of measurements in which the quantities of ammonia solution added differed by smaller increments (0.5 cc.). This showed that the curve has a minumum. In a further series of measurements having a still smaller increment of ammonia solution (0.1 or 0.2 cc.) the region of this minimum was more carefully investigated. In this series the original ammonia solution was diluted ten times and so 0.1 or 0.2 cc. of the original solution correspond to 1 or 2 cc. of the diluted solution. In Table III the measurements are given and in Fig. 3 the conductivities are plotted against the number of cc. of the diluted ammonia solution.

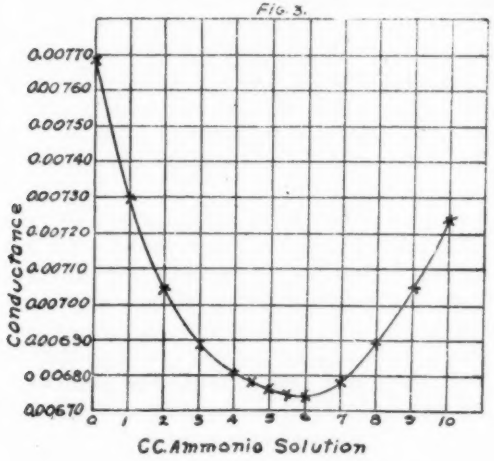
TABLE III.

Solution no.	Ammonia cc.	Conductivity	Solution no.	Ammonia cc.	Conductivity.
1.....	0.00	0.00768	8.....	5.50	0.00674
2.....	1.00	0.00730	9.....	6.00	0.00674
3.....	2.00	0.00704	10.....	7.00	0.00678
4.....	3.00	0.00689	11.....	8.00	0.00689
5.....	4.00	0.00681	12.....	9.00	0.00705
6.....	4.50	0.00678	13.....	10.00	0.00724
7.....	5.00	0.00676			

With a strong acid at great dilution successive additions of ammonia (or any other base) would lower the conductivity, due to

the displacement of the exceedingly mobil hydrogen ion by the slower moving ammonium ion. With a weak acid, however, two

Fig. 3.



opposing factors enter, the hydrogen ion being being replaced, as before, by the ammonium ion, and also the salt having a far higher degree of dissociation than the acid. The second factor is probably the predominant one and slight additions of ammonia would increase the conductivity. Should the citric acid contain a minute amount of a strong acid, the strong acid would be neutralized first, and thus give a minimum conductance. Whether this minimum be due to impurities, or whether other weak bases and weak acids exhibit the same phenomenon is still under investigation in this laboratory.

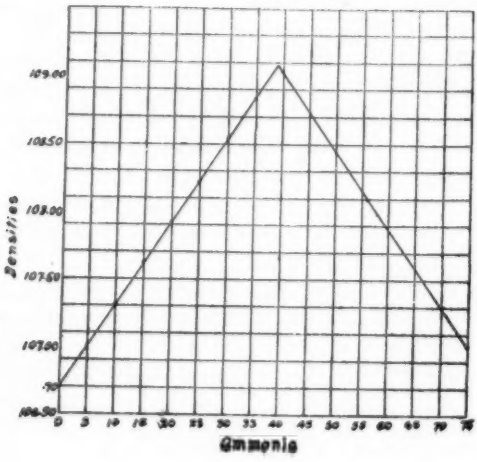
Another method of determining the neutral point of ammonium citrate solution was suggested by the fact that chloroform dissolves free ammonia[1] but does not dissolve citric acid or ammonium citrate and therefore may be used as an agency for removing NH_3

1. Hantzsch and Sebaldt, *Z. physik. Chem.*, 30, 266 (1899); Abbott and Bray, *J. Am. Chem. Soc.*, 31, 729 (1909).

from its salts, if ammonia be present in excess. A series of nine solutions, containing 35, 36, 37..... 43 cc. of ammonia solution, respectively, was prepared, and each solution shaken with chloroform. The chloroform extracts from the solutions containing 35 to 39 cc. of ammonia solution showed no free ammonia on titration with dilute sulfuric acid, methyl orange being used as indicator. The extracts from solutions containing 40 to 43 cc. of ammonia solution contained increasing amounts of free ammonia. Thus the presence of free ammonia in the citrate solution may be detected by shaking out with chloroform and testing the chloroform layer for free ammonia. This offers another method for establishing the end point when citric acid is being neutralized by ammonia.

A series of measurements of the densities of solutions containing citric acid and ammonia offer further confirmation of the position of the neutral point. In preparing these solutions 50 cc. of citric acid solution were placed in a 100 cc. measuring flask and ammonia was added. Water was then added to the mark and the flask and contents weighed and the density computed in the usual way. In Table IV the data thus obtained are given, and in Fig. 4, the

Fig. 4.



number of cc.of ammonia solution is plotted against the densities. It is seen that the neutral solution has the maximum density and that this solution is the same as that indicated by the break in the curve obtained by the conductivity method.

TABLE IV.

Solution no.	Ammonia solution cc.	Density	Solution no.	Ammonia solution cc.	Density
1.....	0	1.0670	7.....	30	1.0853
2.....	5	1.0700	8.....	35	1.0883
3..	10	1.0731	9.....	40	1.0903
4.....	15	1.0762	10.....	45	1.0874
5.....	20	1.0792	11.....	50	1.0864
6.....	25	1.0822	12.....	75	1.0702

SUMMARY

In this paper it has been shown that the neutral point for a weak acid and a weak base, such as citric acid and ammonia may be accurately determined by conductivity measurements; that the presence of an excess of ammonia in the ammonium citrate solution may be ascertained by shaking out with an immiscible solvent, as chloroform, which dissolves a part of the excess of the base but neither the free acid nor the salt; and that the neutral point of the ammonium citrate solution may also be established by density determinations.

CHAPEL HILL, N. C.

PREPARATION OF NEUTRAL AMMONIUM CITRATE SOLUTIONS BY THE CONDUCTIVITY METHOD*

BY ROBERT A. HALL.

In their investigations of the properties of aqueous solutions containing ammonia and citric acid,[1] Hall and Bell found that the neutral point of the solution could be detected by conductivity measurements, and this suggested the application of the conductivity method as a possible means of preparing the neutral ammonium citrate solution required in fertilizer analysis for the determination of the citrate-insoluble phosphoric acid in a fertilizer. In order to ascertain the possibility of readily and easily preparing neutral ammonium citrate by the application of the conductivity method the following experiments were made by the author of this article.

A citric acid solution was prepared of such a citrate content that when neutralized by ammonia its specific gravity would be greater than 1.09 at 20°; that is, 370 grams of pure citric acid[2] were dissolved in ammonium hydroxyde of 0.90 sp. gr. and water, until the solution was near the point of neutrality, yet leaving the solution acid to litmus paper. Care was taken that the volume was not over one liter. The solution was allowed to stand over night to cool. It was again tested with litmus paper to see that it was distinctly acid. Also, small portions, one to two cc., were withdrawn with pipettes and roughly titrated with a diluted ammonia solution in order to ascertain the approximate amounts of ammonia solution necessary to make the citrate solution distinctly alkaline to litmus. The diluted ammonia solution used was prepared by taking the concentrated ammonium hydroxide, sp. gr. 0.90, and diluting exactly exactly ten times, that is, 100 cc. were diluted to one liter. A sufficient amount of this solution was prepared to have enough for the making of the solution for the conduc-

*Reprinted from the Journal of Industrial and Engineering Chemistry, Vol. 3 No. 8. August, 1911.

[1] *J. Am. Chem. Soc.*, **33**, 711.

[2] Method of Analysis; *Bull.*, **107**, Bureau of Chemistry, p. 1.

tivity measurements and also for addition to the larger bulk of the acid ammonium citrate solution, of the calculated amount of ammonia solution as shown by the conductivity measurements, for complete neutrality. 100-cc. lots of the nearly neutralized ammonium citrate solution were withdrawn with pipettes and put in 200 cc. volumetric flasks. Definite amounts of the diluted ammonia solution were measured into these different flasks. Water was then added to the mark, the solution thoroughly mixed, and the flasks placed in an electrically controlled thermostat. The temperature of this thermostat was maintained at 25°, plus or minus 0.01°. When these solutions had come to the temperature of the bath their conductivities were determoned with a Wheatstone bridge in the usual way. The conductivity cell used was the H. C. Jones type for concentrated solutions. The conductances were plotted against the cc. of the ammonia solution used. It was easy to read from the curve thus obtained the number of cc. of the ammonia solution needed to neutralize exactly 100 cc. of the acid ammonium citrate solution used. This amount of the diluted ammonia solution was then measured into a 200 cc. flask containing 100 cc. of the citrate solution and water added to the mark. After thorough mixing, the flask was placed in the bath and allowed to come to bath temperature. Its conductivity was then ascertained. Its conductance showed it to have the amount of ammonia necessary for exact neutralization. The solution, when tested with corallin, methyl orange, methyl red, and neutral litmus paper (Squibb's), gave no evidence of the presence of either acid or base. Also, the solution was shaken out with chloroform, the chloroform separated from the citrate solution and shaken with water and the water tested for ammonia.[1] No ammonia was found. Hence it was concluded that a neutral ammonium citrate solution had been prepared with accuracy and certainty.

Specific gravity determinations were also made of the solution used in these conductivity determinations and the densities plotted against the cc. of ammonia. The curve showed that the neutral solution as prepared by the conductivity curve had the highest specific gravity.[1]

[1]Hall and Bell, *Loc. cit.*

In Table I is given the data obtained in these measurements, and in Fig. 1 the conductanees are plotted against the cc. of ammonia solution used.

TABLE I.

Solution No.	Cc. ammonia.	Conductivity.
1	0.00	0.004085
2	6.00	0.004353
3	18.00	0.004900
4	24.00	0.004997
5	30.00	0.004991
6	40.00	0.004980
7	20.30	0.004999

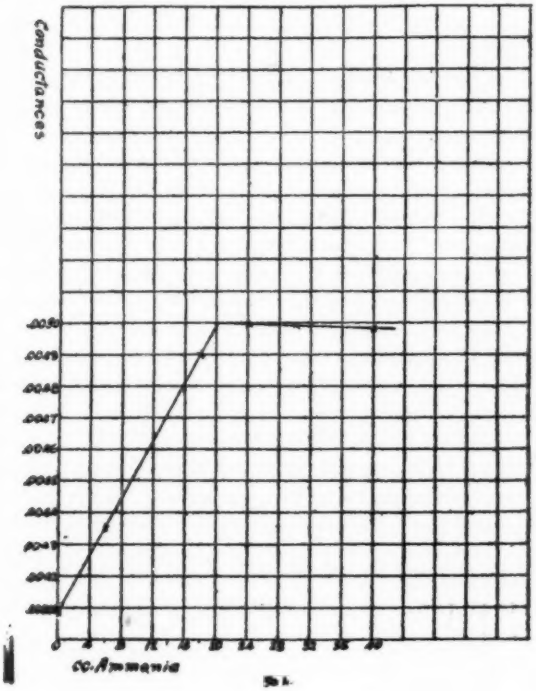


Fig. 1.

The neutral solution as prepared above had a specific gravity greater than 1.09 at 20°. It was therefore an easy matter to dilute with distilled water and in the usual way bring to the required density.

In order to investigate the possibility of the use of the conductivity method of preparing neutral ammonium citrate solution by the chemist who has not the use of an electrically controlled thermostat, or a thermostat regulated by any other method wherein a constant temperature is secured, a series of experiments were made in which the use of the regulated thermostat was dispensed with; that is, the electrical control was cut off and the temperature of the bath allowed to vary with that of the room. However, a time of experimentation was chosen so that there was a minimum of variation of room temperature. In brief, the experiments were conducted under such conditions as can be had in any laboratory where a room fairly well protected from the usual weather variations and from the presence of those entering and leaving the room during the time of the experiment can be had. In the place of the thermostat a tub of water could have been used for the bath.

The solutions were prepared as above, placed in the bath and allowed to come to the temperature of the bath. Erlenmeyer flasks of suitable volume and of such sized mouth as to admit of easy entrance of the electrodes of the cell were placed in the bath, so that when the solutions were being changed in the cells the electrodes could be placed in these flasks and be kept at the temperature of the bath, thus preventing the slight lowering of temperature due to the evaporation of the water on the electrodes. The conductivity measurements were made as rapidly as possible (each was run in less than one and one-half hours), the cells and electrodes being carefully washed each time with the new solution. This rinsing was repeated three times for each change of solutions. During the short intervals of waiting necessary for the cell and its solution to come to bath temperature again after the handling the conductances were computed and the curve plotted, so that as soon as possible after the last point in the curve was located and the curve completed. It was found further that by plotting the bridge

readings against the cc. of ammonia solution used that the same results were obtained as by plotting the conductances against the cc. of ammonia solution. In this way it was possible to make the series of six measurements in a very short time, usually less than one and one-half hours being required, and thus minimize the probability of any great change of room temperature. From the curve was read the amount of ammonia solution needed to be added to 100 cc. of the acid ammoninm citrate in order exactly to neutralize it. This amount of ammonia was run into a 200 cc. flask containing the solution previously measured out, water added to the mark and the solution thoroughly mixed. The flask was then placed in the bath and brought to the temperature of the bath. The conductivity measurement was then made. It was found that the bridge reading obtained corresponded exactly to the bridge reading on the curve for neutral ammonium citrate solution. The same amount of ammonia was then run into another 100 cc. lot of the ammonium citrate solntion and this solution made up a specific gravity of 1.09 at 20°. When these solutions were tested with indicators and chloroform, as above, they gave no evidence of containing either acid or free ammonia in access.

The bath was now brought again to a tempergture of 25° and maintained their by the electrical control while the conductivity measurements were repeated. These gave a curve showing the neutral point to be the same as that found at room temperature.

In Table II are given the data of the measurements made at room temperature. In Fig. 2 the bridge readings are plotted against the cc. of ammonia solution used:

TABLE II.

Solution No.	Cc. ammonia.	Bridge-reading.
1	0.00	49.40
2	10.00	52.01
3	18.00	54.09
4	24.00	54.80
5	30.00	54.75
6	36.00	54.70
7	20.80	54.84

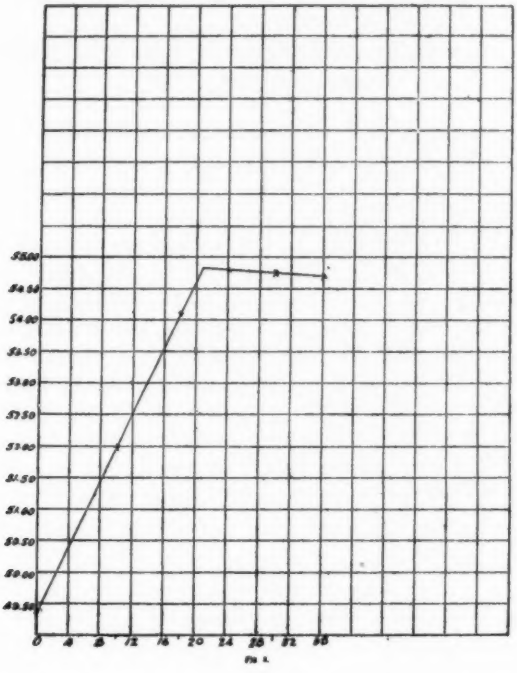


FIG. 1.

An effort was made to ascertain the possibility of preparing a neutral citrate solution by adding an excess of ammonia and afterwards removing this excess by extractions with chloroform.[1] Although repeated extractions were made, there was always free ammonia remaining in the citrate solution. This was to be expected as the ammonia is so much more soluble in water than in the chloroform. Moreover, had it been possible to extract all the free ammonia from the solution the chloroform that would have remained in solution in the citrate solution would have precluded the use of this method for the preparation of neutral ammonium

[1]Hall and Bell, *Loc. cit.*

citrate for the fertilizer analysis, as the chloroform would be decomposed, forming free hydrochloric acid, which would interfere with the determination of the citrate insoluble phosphoric acid.

CONCLUSION

It has been shown that the conductivity method of preparing neutral solutions is applicable to the preparation of exactly neutral ammonium citrate solutions of such a density that they can after neutralization, be diluted with distilled water and brought to a density of 1.09 at 20°. This method can be applied under conditions such as can be easily obtained in any laboratory and therefore seems worthy of adoption as an "Official Method" of preparing the exactly neutral ammonium solution required in fertilizer analysis for the determination of the citrate insoluble phosphoric acid content of the fertilizer. For the regulated thermostat there may be substituted a tub of water. However, a thermostat of constant temperature is preferable, for then there is no necessity of the measurements being carried out so quickly as when the measurements are made in a bath at room temperature.

CHAPEL HILL, N, C.

THE DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM.*

BY JAMES M. BELL AND ALEXANDER L. FEILD.

The distribution of ammonia between water and chloroform has been studied by several investigators. The results have been employed to determine the concentration of free ammonia in an aqueous solution, which contains also some compound of ammonia, such as the blue cuprammonia compounds and the phosphates of ammonium. Until recently the distribution was determined only for dilute solutions, where the concentration of ammonia in the water layer was not greater than normal.

Hantzsch and Sebaldt[1] found that the ratio of the concentrations of ammonia in water and chloroform is 25.1 at 25°, the mean of five determinations in which the concentration in the water layer varies from 0.00275 to 0.04425 normal. At 2° this ratio is 38:53. Dawson and McCrae[2] give the following values for the distribution ratio: 26.3 at 20°, 24.9 at 25°, and 23.2 at 30°, the highest concentration in the water layer being 14.14 grams NH_3 per liter. In a later paper Dawson and McCrae[3] repeated their determinations at 20°, the extreme concentrations of ammonia in the water layer being being 5.160 and 17.168 grams NH_3 per liter. Between these limits the distribution ratio is not quite independent of the ammonia concentration. The ratio varies from 26.36 for the most dilute solution to 25.32 for the most concentrated.

The following quotation is from a later paper by Dawson:[4] "In reference to the distribution of ammonia between pure water and chloroform, it has already been shown that the concentration ratio H_{H_2O}/C_{CHCl_3} decreases with increasing ammonia concentra-

*Reprinted from The Journal of The American Cnemical Society, Vol. XXXIII. No. 6. June, 1911.

[1] *Z. physik. Chem.*, **30**, 258 (1899).

[2] *J. Chem. Soc.*, **77**, 1239 (1900).

[3] *J. Chem. Soc.*, **79**, 493 (1901).

[4] *J. Chem. Soc.*, **89**, 1668 (1906)

tion, but the relationship between these two factors could not be determined with a desirable degree of accuracy in the case of dilute solutions containing less than 0.5 mol. of ammonia per liter of aqueous solution." Consequently new determinations were made at 19.5° by an improved method. Representing k (the distribution rato) as a function of c' (the concentration in the chloroform layer) the points so obtained lie approximately on the straight line corresponding to the equation

$$k = 26.16 - 34.14c'.$$

Abbott and Bray[1] have also found the distribution ratio with the object of determining the degree of hydrolysis of several phosphates of ammonium in aqueous solution. At 18° the ratio is 27.45, where the aqueous layer has a concentration between 0.02 and 0.05 normal.

In more concentrated ammonia solution , Dawson[2] has found that at 18° the distribution ratio decreases from 26.46 at 0.928 normal to 21.70 at 4.333 normal.

The present paper contaius the results of an investigation of this distribution at 25° and over a much wider range of concentration. Chloroform was added to aqueous solutions of ammonia of varying strength. The bottles were placed in an electrically heated and controlled thermostat at 25° and were frequently shaken. When equilibrium had been reached, a known volume of each layer was titrated against standard acid. The following table contains the concentration of ammonia in each layer expressed in gram molecules per liter and also the distribution ratio between the two layers.

It will be seen from the table that the distribution varies from 22 in dilute solution to about 10 in concentrated solution. The limit to which the distribution tends at very great dilution appears to be about 24.

TABLE I.

Normality NH_3 in water layer. c	Normality NH_3 in $CHCl_3$ layer. c'	Distribution ratio. k
1.02	0.045	22.7

[1] *J. Am. Chem. Soc.*, **31**, 729 (1909).

[2] *Z. physik. Chem.*, **69**, 110 (1909).

2.08	0.095	21.9
3.13	0.146	21.4
3.98	0.205	19.4
5.24	0.283	18.5
6.25	0.365	17.1
7.29	0.457	15.9
8.34	0.549	15.2
9.35	0.710	13.2
10.23	0.864	11.8
11.24	1.045	11.0
12.23	1.227	10.0

The following table contains the limiting values of the distribution ratio for very dilute solutions as found at different temperatures by the various workers in this field.

TABLE II.

Temp.	Dist. Ratio.	Observer.
2°	38.5	Hantzsch and Sebaldt.
18	27.45	Abbott and Bray.
18	27.5 approx.	Dawson.
20	26.5	Dawson and McCrae, I.
20	25.3	Dawson and McCrae, II.
25	25.1	Hantzsch and Sebaldt.
25	24.9	Dawson and McCrae, I.
25	24. approx.	Bell and Feild.
30	23.2	Dawson and McCrae, I.

The accompanying table (II) shows clearly that the distribution ratio falls as the temperature rises.

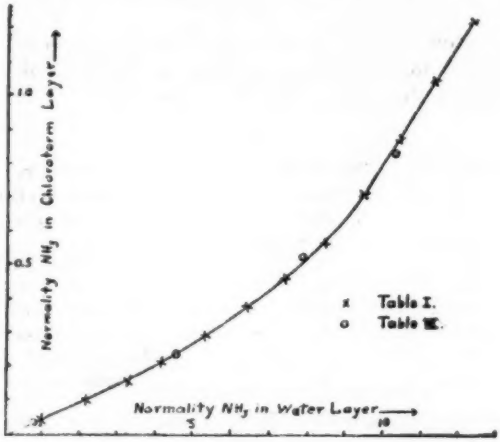
The points obtained by plotting the values of C and K in Table I lie on a curve which deviates rather far from a straight line, so that the formula given by Dawson holds only for the more dilute solutions, and is of value in giving the limiting direction of the curve. This result is confirmed by the later results of Dawson where more concentrated solutions have been used.

The effect of other compounds on the distribution ratio has been investigated by Hantzsch and Sebaldt[1] and by Dawson and McCrae.[2] As ammonia is a weak base it is but slightly ionized

[1] *Z. physik. Chem.*, **30**, 258, (1899).

[2] *J. Chem. Soc.*, **79**, 493 (1901).

even at great dilutions, and consequently the addition of an ammonium salt would increase the number of undissociated molecules very slightly, while the percentage decrease of ionization would be greatly diminished. If unionized ammonia is the substance distributed, then the presence of ammonium chloride should affect the distribution very slightly and then only on account of the "salting out" effect. If, on the other hand, the ionized portion were distributed, the presence of the highly ionized salt would affect the distribution very greatly. In very dilute



solutions Hantzsch and Sebaldt have found that ammonium chloride has almost no effect. Dawson and McCrae have, however, shown that the effect is measurable, the distribution ratio at 20° decreasing by 0.88 for each mol. of salt per liter of solution. The nitrate and sulfate also lower the distribution ratio, while the bromide increases it. The following table (III) gives the results of experiments on the distribution of ammonia between chloroform and a solution of ammonium chloride containing about 3 mols. per liter. At each concentration of ammonia the distribution ratio is very close to that found in the absence of ammonium chloride.

TABLE III.

Normality NH_3 in water layer (NH_4Cl—3N)	Normality NH_3 in $CHCl_3$ layer calc.	Normality NH_3 in $CHCl_3$ layer obs.
0.84	0.037	0.037
4.32	0.226	0.228
7.72	0.494	0.512
10.16	0.837	0.820

In this paper it has been shown that at 25° the distribution ratio for ammonia between water and chloroform varies with the concentration, from about 24 in dilute solution to about 10 in concentrated solution. The presence of ammonium chloride affects the distribution very slightly.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C.

SOME PLUTONIC ROCKS OF CHAPEL HILL

BY WILLIAM H. FRY

The Chapel Hill area is situated in the northern central part of the state in the "Carolina Metamorphic Slate and Volcanic Belt." The area here considered is bounded on the south by igneous slates of unknown age generally spoken of as the Purefoy's Mill series; on the southeast, east, and northeast by Triassic sandstones; and on the north and west by very basic crystalline plutonics and acid volcanics of comparatively recent age, probably triassic, as bombs of the material are found embedded in the sandstone to the east. The rocks composing the area are mainly granites, the exceptions being small dikes of a diabasic nature. Watson, Laney, and Merrill[1], describe the field appearance and locations of the plutonics of the area as follows:

"Boulders and ledge outcrops of granite are exposed along Bolans creek where crossed by the Durham road, one mile northeast of Chapel Hill, near the contact of the crytalline rocks with the Triassic sandstones. The rock indicates much variation in texture from a very fine grained even granular granite of a decided pink color. Reddish pink feldspars, quartz and a small quantity of biotite are apparent to the unaided eye. The rock is entirely massive and is intersected by several sets of joints. No attempt has been made to quarry the stone and its marked variable texture would make it undesirable as a general building stone.

"The outcrop on the Clayton place on the north side of Brocker's creek, one and a half miles north of Chapel Hill, shows more or less variation in texture and color, though the rock is usually dark gray and of a very fine texture. No statement can be made of the working qualities of the stone.

"Four miles north of Chapel Hill and 150 yards east of the railroad is an exposure on the Brocker place, of pinkish gray granite with porphyritic tendency, containing large laths of pink

[1]Bulletin 2, N. C. Geol. Survey, 1906.

feldspar. It lacks uniformity in both color and texture and for this reason would not prove a very desirable stone for general building purposes."

The only previous petrographic work done on the area consists of two papers published by Mr. H. N. Eaton; one a description of micropegmatite in a binary granite[1], the other a few petrographic descriptions of some of the granites of the area[2].

In the introduction to the latter paper he speaks of the area as follows:

"The village of Chapel Hill, North Carolina, is located upon a gently rounded knob of granite rocks.....Northward the granite becomes rapidly more basic, reaching a quartz-mica-diorite, or grano-diorite. Rocks resembling true diorites macroscopically are adjacent on the north. Aplite dikes exist everywhere, and a suite of specimens can be easily collected showing a gradation from this binary type to rocks containing biotite and hornblend. The range in color varies from fine grained, white, acid rocks, to those which are dark, medium, and coarse grained." He then gives descriptions of a few specimens and their sections.

A large number of samples have been collected by the present writer representing the area more thoroughly than did the specimens collected by Mr. Eaton. Thin sections were made from representative types of these samples. Descriptions of these thin sections and the specimens from which they were taken are given below.

I.—This rock occurs under the railroad bridge about one and a fourth miles north of the station, near the old iron mine. In hand specimen it is rather fine grained; rather dark in color, and weathers to a brownish dirty-looking soil belonging to the Iredell series. It is mottled with greenish hornblende and light feldspar.

The thin section contains magnetite, feldspar, hornblende, and quartz. The magnetite is abundantly present in comparatively small scattered granules. The feldspar is very much decomposed. The main mass of it is probably orthoclase, judging from its crys-

[1]Jour. Elisha Mitchell Scientific Society, Vol. 24, No. 3, Nov. 1908.

[2]Jour. Elisha Mitchell Scientific Society, Vol. 25, No. 3, Nov. 1909.

talline outlines. Other weathered feldspars are present, most of them probably one or more of the plagioclases. One plagioclase crystal was fresh enough for determination as labradorite. The hornblende is green in color, and is segregated into clusters mixed with magnetite, and alone. Quartz is abundantly scattered through the whole section. The rock was determined as hornblende granite.

II.—In handspecimen the rock is very finely crystallized. The color is a sort of white tinged with brown. The fracture is conchoidal althougn the rock is not so fine grained as to be cryptocrystalline. Altogether the rock has a very pronounced quartzitic appearance. It occurs about half a mile northeast of Piney Prospect in Strowd' field at the contact between the crystalline rock and the Triassic sandstone.

The thin section contains hornblende, magnetite, quartz, orthoclase, and tourmaline. The hornblende occurs sparingly scattered through the section. The magnetite is present in occasional grains. Quartz is the predominating mineral, and is intermixed with a considerably less amount of orthoclase. The tourmaline is present in small scattered grains. It doubtless owes its origin to the action of magnetic gases near the periphery of the intrusion. The rock was determined as a hornblende granite.

III.—Macroscopicolly the rock is fine grained, light with a tinge of pink in color, and very closely jointed, breaking into rhombohedra-like forms. It occurs near the Raleigh road about one fourth of a mile out from the cemetery.

The thin section contains quartz, plagioclase, hornblende, and magnetite. The quartz is abundantly present in comparatively large granules. The plagioclase feldspar is sparingly scattered through the section in very small granules. The orthoclase is slightly weathered, and is present in large masses. The hornblende is present only in a very slight amount. The magnetite is present in medium sized and scattered granules. The rock was determined as hornblende granite, almost a binary type of granite.

IV.—This rock is very fine grained, almost cryptocrystalline. It is slightly darker in color than usual and has a greenish ap-

pearance. It occurs on the Hillsboro road just north of Bolin's creek.

The thin section contains apatite, hornblende, quartz, plagioclase, and orthoclase. Apatite was located in only one place, and occurred in the form of an acicular crystal. The hornblende is scattered through the section. In one case it is segregated into a large nodule. Laths of plagioclase feldspar are abundant; while only a slightly smaller quantity of orthoclase is present. The quartz occurs mainly as the filling of a vein which traverses the section. Outside of the vein quartz, while still present, does not constitute the main mass of the rock. Along one plane of the section a slight normal faulting has taken place. The rock was determined as hornblende granite.

V.—This rock is of a light flesh-colored pink. The grains are medium sized. The rock is splotched with a greenish mineral. It occurs to the northwest of the hosiery mill about one half of a mile.

The section contains quartz, plagioclase, feldspar, hornblende, magnetite, and orthoclase. The quartz is present in large, irregular, and apparently stressed crystals. Some of them are filled with minute cavities and inclusions of other minerals. The plagioclase is oligoclase. Much slightly decomposed hornblende is present, and is usually segregated into particular localities. The magnetite is present only in very slight amounts. The orthoclase is not predominant. The rock was determined as hornblende granite.

VI.—In handspecimen this rock is medium grained, light pink in color, and breaks with a conchoidal fracture. It occurs on the old Durham road near its junction with the new road on the south side of Bolin's creek.

The thin section contains quartz, hornblende, and oligoclase. The quartz is present in predominating quantities. The orthoclase is abundant and is very much kaolinized. The hornblende occurs in a seam running completely through the section, with a little quartz intermixed with it. Outside the seam the hornblende is present only in very meager amounts. The oligoclase occurs as

a few scattered crystals. The rock was determined as hornblende granite.

VII.—This rock is very coarsely crystalline. It is dark green in color mottled with white and pink feldspars. It occurs south of the Raleigh road near the cemetery. The section contains hornblende, magnetite, quartz, labradorite, orthoclase, and biotite. The hornblende is present in large amounts as small scattered crystals. The magnetite is present in very small quantities. The quartz occurs filling the interstices between the other minerals. Labradorite is present in small quantities. Orthoclase is the prevailing feldspar, and occurs in large crystals, almost phenocrysts. Biotite is present in very small amounts. It is brown in color. The rock was determined as hornblende-biotite granite.

VIII.—This rock is medium grained in texture and light gray in color. Macroscopically a flake or two of biotite were noticed. but the mineral was in negligable quantities. None was located in this section. The rock occurs on the campus of the University of North Carolina near the athletic field.

The section contains orthoclase, hornblende, chlorite, quartz, and magnetite. The quartz is the predominant mineral and occurs in large, well defined crystals. The orthoclase occurs as crystals which are much kaolinized and are almost phenocrysts in certain cases. The hornblende is in small scattered crystals occupying a very inferior area of the section. It is greenish and brownish in color. The chlorite is green and probably represents a decomposition product. The magnetite occurs very sparingly in small scattered masses. The rock was determined as hornblende granite.

IX.—This rock is very fine grained macroscopically. The color is very light gray. The rock occurs on the Pittsboro road about a mile out from the Chapel Hill public school.

The thin section contains quartz, hornblende, feldspars, and magnetite. The quartz occurs as phenocrysts scattered through a groundmass composed of the other minerals present, and as small crystals composing a part of the groundmass. The crystals are studded with gas bubbles. A rather large veinlet is filled with quartz. The hornblende occurs in rough, irregular patches and

stringers. The crystals individually are very small. A small vein running nearly across the section has hornblende for its vein material. The feldspar is probably a mixture of orthoclase and one or more of the plagioclases. The crystals are very small, but show good crystalline outlines between crossed nicols. The shapes are rather elongate The magnetite occurs very sparsely as small granules. The rock was determined as hornblende granite.

X.—This is a very fine grained and light colored rock. It occurs on the Chatham road near its junction with Cameron Avenue.

The section contaihs quartz, hornblende, and feldspar. The quartz occurs as large phenocrysts and occupies the larger portion of the section. In several instances good hexagonal outlines were observed. A large sized veinlet filled with quartz extends nearly across the section with somewhat of a crank-shaped course. The outline between the vein and the wall is very clearly drawn. In some cases horses of the groundmass of the rock occur in the vein. The vein was evidently formed by some mechanical disturbance and filled by silica-bearing solutions. The hornblende occurs in stringers and small scattered crystals. The stringers in one locality are all sheared and drawn out in parallel directions, indicating some mechanical disturbance. The feldspar is very fine grained and is probably orthoclase. It forms the main groundmass material of the section. The rock was determined as hornblende granite.

XI.—This is a medium grained and quartzitic-appearing rock. The color is a very light pink. Macrascopically the rock appears to be almost a binary type. It occurs to the north of Chapel Hill near the "Colorado Canon."

The thin section contains quartz, orthoclase, magnetite, hornblende, chlorite, plagioclase, and a negligible quantity of biotite. The quartz occupies the major portion of the section. It occurs in large, well developed, and apparently stressed masses. The orthoclase occurs in masses somewhat larger than those of the quartz. It is slightly kaolinized. Pieces showing good crystalline outlines are rare. It is also apparently stressed. The magnetite occurs in small scattered masses occupying a very inferior portion of the section. The hornblende occurs scattered promiscuously

through the rock, seldom in large masses. Chlorite was observed in one instance as a small, ill-defined mass. It is probably a decomposition product. The plagioclase is probably labradorite. It was observed in only one locality. The crystal was very small and irregular. The rock was determined as hornblende granite.

XII.—This rock is very coarse grained and very dark in color, mottled with green. It occurs to the north of Chapel Hill on the the hill north of the Oxford road.

The thin section contains quartz, hornblende, orthoclase and magnetite. The quartz occurs in well defined crystals often showing hexagonal outlines The crystals show a tendency to segregation in small masses. The hornblende occurs in clearly marked crystalline forms with well marked cleavage. It is greenish and brownish in color. The orthoclase is slightly kaolinized and shows no crystalline form. It occurs in large masses intermixed with the hornblende. The magnetitite occurs in small scattered granules. The rock was determined as hornblende granite.

XIII.—This rock is rather coarsely crystalline and of a deep pink color. The fracture is sub-conchoidal. It occurs in Battle's Park south of the Dissecting Hall.

The section contains quartz, orthoclase, plagioclase, hornblende, magnetite, and biotite. The quartz occurs in large irregularly shaped masses seldom showing any distinct crystalline outlines. The plagioclase is labradorite. It occurs sparingly scattered through the section in well defined crystalline forms, and shows perfect twinning. The hornblende occurs in small segregated masses and fairly well defined crystals of medium size scattered promiscuously through the rock. In some instances the cleavage can be observed, but not without difficulty. The magnetite occurs more abundantly than usual as medium sized but scattered granules. It occupies only an inferior portion of the rock section. Biotite occurs sparingly in small scattered flakes. The cleavage can usually be made out. It is brownish in color. The rock was determined as hornblende-biotite granite.

XIV.—This is a very coarsely crytalline rock. The color is light gray mottled with black. It occurs in the alley near the residence of Mr. H. H. Patterson on Cameron Avenue. The rock

is very much decomposed.

The section contains quartz, orthoclase, hornblende, and magnetite. The quartz occupies the major portion of the section, and occurs in masses which are almost phenocrysts. The crystals are intergrown with each other in a remarkably irregular manner. The orthoclase occurs in large masses, and in some of these the cleavage can be very well observed in spite of the decomposed condition of the mineral. In one case a perfect crystal of orthoclase was found imbedded in an irregular mass of the same mineral. The hornblende shows a marked tendency to segregation into large bunches. It is green in color, and in the individual crystals, the cleavage can be made out fairly well. The magnetite, as usual, occurs in small sized, scattered granules usually, but not always, associated with the hornblende. The rock was determined as hornblende granite.

XV.—In handspecimen this rock is very coarsely granular. In color it is light gray splotched with black. It occurs on Franklin street near the residence of Prof. E. V. Howell. The sample was collected from an excavation made for sewerage. When exposed the rock is very much decomposed.

The thin section contains quartz, orthoclase, hornblende, and magnetite. The quartz occurs in large grained, irregular masses occupying probably half of the section. The orthoclase is very much kaolinized, but shows good crystalline outlines. It occurs in large crystals. The hornblende occurs in abundance. It is greenish in color and shows practically absolutely perfect cleavage. The magnetite occurs in irregularly scattered granules. The rock was determined as hornblende granite.

Out of the nine granites described by Mr. Eaton in the papers already referred to only one was a hornblende granite, two were binary granites, one a muscovite granite, one a biotite-hornblende granite, and four were biotite granites. These cover pretty thoroughly the types of acid plutonics found in this area; but the papers give a wrong conception of the relative proportions of each type. In the present paper, out of fifteen sections described, thirteen were hornblende granites, while the other two were horn-

blende-biotite granites. It is thought, both from field evidence and from the present work, that this latter proportion comes nearer being representative of the acidic area than does the former. The biotite granites undoubtedly exist here, but seldom without a great deal of hornblende intermixed. The muscovite and binary granites must be considered as rare exceptions.

MINERALS OF THE CHAPEL HILL REGION

BY WILLIAM H. FRY.

The following minerals are known to occur in the Chapel Hill area: gold, pyrrhotite, pyrite, quartz, flint, hematite, magnetite, some manganese minerals, limonite, orthoclase, microcline, oligoclase, andesine, labradorite, augite, hornblende, zircon, epidote, tourmaline, muscovite, biotite, chlorite, prochlorite, serpentine, talc, kaolinite, titanite, apatite. Many more are doubtless present, but so far they have not been brought to light.

Gold occurs in a quartz vein about two and one half miles north of the village of Chapel Hill. The vein runs in a north to northeast and southwest direction. The material has been assayed and was found not to be economically valuable.

Pyrrhotite has been determined by the writer from specimens collected in the dump heaps of the old Chapel Hill iron mine. It is of very rare occurrence in this locality.

Pyrite occurs rarely in material from the iron mine. In some cases it carries a trace of copper. As a magmatic segregation it is found rather abundantly in connection with the basic plutonics of the area. As an accessory mineral it occurs in practically all the igneous rocks of the neighborhood.

Quartz, besides its occurrence as a rock constituent, is found in numerous veins. These range in width from a fraction of an inch to sometimes several feet. Here the mineral is undoubtedly an aqueous precipitate. Beautifully formed crystals are occasionally found in geodes of the country rock. The flint of the area is of doubtful nature. It seems to be a very acid volcanic rock rather than the true mineral.

Hematite is found abundantly at the Chapel Hill iron mine where it was formerly worked. The ore[1] has been considered as the filling of an ordinary fissure vein. Analyses of some of the ore from the mine are as follows[2]:

Magnetite occurs admixed with the other iron ores of the Chapel

[1] Nitze, Bull. 1, N. C. G. S.

[2] Roberts, J. C., this Journal, 1883-'84, pp. 26-27.

Hill mine, as an accessory rock constituent, and float ore. Writing of this float ore John L. Borden[1] has the following:

"This magnetite is found on the farm of—Cheek, about three miles south of Chapel Hill. Pieces ranging up to ten or fifteen pounds in weight are found scattered over the field. One of these was analyzed with the following result:

Magnetic iron oxide	96.03
Silica	3.02
Water	.52
Sulphur	.19
Phosphorus	trace
	99.76"

Manganese minerals[2] occur admixed with limonite in Strowd's field. "The formation is similar to the formation of bog iron ore. There is only a small quantity of the ore, scattered on the surface." There is auother occurrence on the Cheek farm somewhat similar to the above. Other small occurrences have been located. The manganese minerals composing the deposits have not been separately determined. They probably consist of the oxides and hydrates.

Limonite occurs abundantly. The ore usually is found in the shape of bog deposits.

Orthoclase, microcline, oligoclase, andesine, hornblende, zircon, epidote, muscovite, biotite, chlorite, titanite, and apatite[3] have been reported as occurring in the granites of the area. In addition to these the writer has found labradorite, augite, and tourmaline in thin sections of the country rocks. The tourmaline occurs in the granites near their contact with the Triassic sandstones.

Prochlorite[4] has been found about one-fourth of a mile from Orange Church north-east of Chapel Hill. It occurs admixed with decomposed muscovite.

Serpentine[5] has been reported from somewhere near Chapel Hill.

[1]This Journal, 1883-'84: p. 87.

[2]Pratt, J. H., Unpublished Notes.

[3]Eaton, H. N., This Journal, Vol. 25, No. 3, Nov., 1909.

[4]Pratt, J. H., loc. cit.

[5]Genth, F. A., "Minerals of North Carolina."

The writer has not been able to verify this occurrence.

Talc occurs rather commonly in connection with the more basic rocks of the area.

Kaolinite, almost pure, was found by the writer about one fourth of a mile to the rear of Mr. Patterson's residence on Cameron Avenue. The deposit covers about five or six square yards.

FORMULAS FOR INVESTMENT CALCULATIONS

BY THOMAS F. HICKERSON

This is an attempt to present clearly and logically all the formulas needed for various interest and sinking fund computations that may come within the field of the engineer. Many of these formulas, in a less general form than given in this paper, have been found here and there in algebras, civil engineering text books and journals, while others have never been seen in print.

SIMPLE INTEREST.

Let P=Principal in dollars.

r=Rate of interest. [Interest on $1 for one year.]

n=Total time in years.

I=Interest on the principal at the end of n years.

A=Amount at end of n years.

Then, $I=Prn$ ..... (1)

Solving for P, r, and n we have

$P=I/rn$; $r=I/Pn$; $n=I/Pr$. ..... (2)

Also, $A=P+I=P+Prn=P(1+rn)$ ..... (3)

Solving for P, r, n and I, we have

$$P=\frac{A}{(1+rn)};\quad r=\frac{(A-P)}{Pn};\quad n=\frac{(A-P)}{Pr};\quad I=\frac{Arn}{(1+rn)}$$

..... (4)

COMPOUND INTEREST.

Interest is compounded when it is added to the principal and becomes a part of the principal at specified intervals.

Let P=Principal in dollars.

r=Rate of interest (Interest on $1 for one year.)

n=Total time in years.

t=Time in years between two successive compoundings; thus, if the interest is to be compounded quarterly, $t=1/4$.

A=Amount at end of n years.

It is evident that the total number of periods [compoundings] equals $\frac{n}{t}$ and the rate per period equals rt.

Amount at end of 1st period $= P+Prt = P(1+rt)$
" " " " 2nd " $= P(1+rt) + P(1+rt) \times rt = P(1+rt)^2$
" " " " 3rd " $= P(1+rt)^2 + P(1+rt)^2 \times rt = P(1+rt)^3$

Hence, the amount at the end of the last or $(n/t)^{th}$ period, in accordance with the above observed law, $= P(1+rt)^{n/t}$.

Hence, we have $A = P(1+rt)^{n/t}$ ..... (5)

If interest is compounded annually $(t=1)$ $\therefore A = P(1+r)^n$
" " " " semi-annually $(t={}^1/_2)$ $\therefore A = P(1+{}^r/_2)^{2n}$
" " " " quarterly $(t={}^1/_4)$ $\therefore A = P(1+{}^r/_4)^{4n}$
etc.

Solving for P and n respectively, we have

$$P = \frac{A}{(1+rt)^{n/t}}; \quad n = \frac{t \times (\log A - \log P)}{\log (1+rt)} \text{ ..... } (6)$$

No simple formulas can be derived for r and t.

If the interest is not compounded annually, we may use tables made for the case when it is compounded annually, as follows: Compute the number of periods (conversions) and the rate per period and use the tables just as though the periods were years and the rate per period were rate per year.

SINKING FUNDS.

A sinking fund is a sum of money which must be set aside at the end or beginning of each successive interval of time (usually at the end of each year) and placed at interest in order to amount to a specified sum in n years.

To Find the Amount of a Sinking Fund.

a) Simple interest basis.

Let S = value of the sinking fund in dollars.
n = number of years.
r = rate of interest.
k = length of time (in years) between payments.
A = amount of sinking fund at end of n years.

Total number of payments $= \frac{n}{k}$

First, suppose payments to be made at the *end* of each period of k years.

A_1 = amount of 1st S in (n—k) years = S+Sr (n—k)

A_2 = " " 2nd S in (n—2k) " = S+Sr (n—2k)

A_3 = " " 3rd S in (n—3k) " = S+Sr (n—3k)

....

$A_{n/k}$ = " " $(\frac{n}{k})$th S in $(n-\frac{n}{k}\times k)$ years = S+0

$\therefore A = A_1+A_2+A_3+ \ldots A_{n/k} = \frac{n}{k}S+Sr\times\frac{n}{2k}(n-k)$ ...(7)

If k = 1, $A = n S + Sr\times\frac{n}{2}(n-1)$.....(8)

Next, suppose the payments to be made at the *beginning* of each period of k years; then it follows similarly that

$A = \frac{nS}{k}+Sr\times\frac{n}{2k}(n+k)$..... .....(9)

If k = 1, $A = n S + Sr\times\frac{n}{2}(n+1)$ ....(10)

The difference between the amounts as given by formulas (7) and (9) equals S r n, which is the interest on S dollars at r per cent for n years.

Example.

$100 set aside at the end of every six months and placed at simple interest at 6 per cent for 10 years will amount to, using formula (7), $2\times10\times100+.06\times10\times9.5 = \$2570$.

If this amount is set aside at the *beginning* of every period of six months, we have, using formula (9):

$A = 2000+100\times.06\times10\times10.5 = \$2630$.

b) Compound interest basis.

Let S, n, r, k, and A represent the same notation as used above. In addition, let t = time in years between successive compoundings of interest.

First, suppose the payments to be made at the *end* of each period of k years.

Amount of 1st S in (n—k) years $= S(1+rt)^{\frac{n-k}{t}}$

" " 2nd " " (n—2k) " $= S(1+rt)^{\frac{n-2k}{t}}$

" " 3rd " " (n—3k) " $= S(1+rt)^{\frac{n-3k}{t}}$

....

" " $\left(\frac{n}{k}\right)$th S in $\left(n-\frac{n}{k}\times k\right)$ years $=S$

$$A=S(1+rt)^{\frac{n-k}{t}}+S(1+rt)^{\frac{n-2k}{t}}+S(1+rt)^{\frac{n-3k}{t}}+\ldots+S$$

Hence, summing up the geometric series, we have

$$A=\frac{S[(1+rt)^{n/t}-1]}{(1+rt)^{k/t}-1} \quad \ldots\ldots\ldots\ldots (11)$$

or $$S=\frac{A[(1+rt)^{k/t}-1]}{(1+rt)^{n/t}-1} \quad \ldots\ldots\ldots\ldots (12)$$

Formula (12) gives the necessary sinking fund to accumulate an amount A in n years, etc.

If k=1, t=1, then

$$A=\frac{S[(1+r)^n-1]}{r} \quad \ldots\ldots\ldots\ldots (13)$$

$$S=\frac{Ar}{(1+r)^n-1} \quad \ldots\ldots\ldots\ldots (14)$$

Next, suppose the payments to be made at the *beginning* of each period, then

$$A=\frac{S[(1+rt)^{n/t}+(1+rt)^{\frac{n-k}{t}}+\ldots.+(1+rt)^{k/t}]=S[(1+rt)^{\frac{n+k}{t}}-(1+rt)^{k/t}]}{(1+rt)^{k/t}-1} \quad \ldots\ldots\ldots\ldots (15)$$

If k=1, t=1, then

$$A=\frac{S[(1+r)^{n+1}-(1+r)]}{r} \quad \ldots\ldots\ldots\ldots (16)$$

The difference between the amounts as given by formulas (11) and (15) equals $S[(1+rt)^{n/t}-1]$, which is the amount of S dollars at r per cent. compound interest for n years.

Example.

$100 set aside at the end of every six months and placed on interest, compounded semi-annually at 6 per cent. for 10 years will amount to, using formula (11), with r=.06, k=½, t=½, n=10, S=100;

$$A=\frac{100[(1.03)^{20}-1]}{.03}=\$2687.03$$

If this amount is set aside at the *beginning* of every period we have, using formula (15),

$$A=\frac{100[(1.03)^{23}-(1.03)]}{.03}=\$2767.64$$

ANNUITY.

An annuity is a fixed sum of money payable at definite intervals of time (not necessarily every year). Evidently an unpaid annuity, with interest, will amount to the same sum as a sinking fund set aside at the same intervals. Hence, the formulas already derived for the amount of a sinking fund are also applicable for finding the amount of an annuity.

PRESENT VALUE OF FUTURE PAYMENTS.

The present value, P, of A dollars payable n years hence is equal to that sum P which when placed at interest for n years will amount to A dollars.

$$\text{Hence, } P=\frac{A}{(1+rt)^{n/t}} \text{ [See formula (6)]} \quad \ldots\ldots\ldots(17)$$

$$\text{If } t=1,\ P=\frac{A}{(1+r)^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots(18)$$

Also, on simple interest basis, we have

$$P=\frac{A}{(1+nr)} \text{ [See formula (4)]} \ldots\ldots\ldots\ldots\ldots(19)$$

The present value, P, of an annuity of S dollars payable at the *end* of every interval of k years for a period of n years with interest compounded at the end of each interval of t years is the *same* as that sum P which, if placed at compound interest, would amount to A dollars, where A equals the amount of the annuity in n years.

$$A=\frac{S[(1+rt)^{n/t}-1]}{(1+rt)^{k/t}-1} \text{ [See formula (11)]}$$

$$A=P(1+rt)^{n/t} \text{ [See formula (5)]}$$

$$\text{Hence, } P(1+rt)^{n/t}=\frac{S[(1+rt)^{n/t}-1]}{(1+rt)^{k/t}-1}$$

$$\therefore P = \frac{S\left[1 - \frac{1}{(1+rt)^{n/t}}\right]}{(1+rt)^{k/t}-1} \quad \text{.....(20)}$$

If k=1, t=1,

$$P = \frac{S\left[1 - \frac{1}{(1+r)^{n}}\right]}{r} \quad \text{.....(21)}$$

The present value of a perpetual annuity ($n = \infty$) equals

$$\frac{S}{(1+rt)^{k/t}-1} = \frac{S}{r} \text{ (if } k = t = 1) \quad \text{.....(22)}$$

Equating formulas (3) and (7) it follows that, on a simple interest basis,

$$P = \frac{\frac{nS}{k}\left[1 + \frac{r}{2}(n-k)\right]}{(1+nr)} \quad \text{.....(23)}$$

$$\text{If } k=1,\ P = \frac{nS\left[1 + \frac{r}{2}(n-1)\right]}{(1+nr)} \quad \text{.....(24)}$$

The present value of an annuity of S dollars payable at the beginning of every period of k years, etc., is

$$P = S\left[\frac{(1+rt)^{k/t} - (1+rt)^{\frac{k-n}{t}}}{(1+rt)^{k/t}-1}\right] \quad \text{.....(25)}$$

$$\text{If } k = 1,\ t = 1, \text{ then } P = \frac{S\left[(1+r) - \frac{1}{(1+r)^{n-1}}\right]}{r} \quad \text{..(26)}$$

If the annuity is perpetual ($n = \infty$),

$$P = \frac{[S(1+rt)^{k/t} - 0]}{(1+rt)^{k/t}} = \frac{S(1+r)}{r} \text{ (if } k=t=1) \quad \text{...(27)}$$

Equating formulas (3) and (9) it follows that, on a simple interest basis,

$$P=\frac{\frac{nS}{k}\left[1+\frac{r}{2}(n+k)\right]}{(1+nr)} \quad \text{.....(28)}$$

$$\text{If } k=1,\ P=nS\left[\frac{\left[1+\frac{r}{2}(n+1)\right]}{(1+nr)}\right] \quad \text{.....(29)}$$

The difference between the present values as given by formulas (25) and (20) equals

$$S\left[1-\frac{1}{(1+rt)^{n/t}}\right]$$

Example.

Find the present value of an annuity of $1 for 20 years with interest at 4 per cent.

Payments at end of each year:

P (Compound interest basis) = $13.59 (Formula 21)

P (Simple " " = $15.33 (Formula 24)

Payments at beginning of each year:

P (Compound interest basis) = $14.13 (Formula 26)

P (Simple " ") = $15.78 (Formula 29)

To find the present value of an annuity which is to begin (a) years hence and continue at the *end* of each interval of time k (in years) for b years, interest being compounded every t years.

The present value of such an annuity, were it to begin k years hence and continue for (a+b) years, equals

$$\frac{S\left[1-\frac{1}{(1+rt)^{\frac{a+b}{t}}}\right]}{(1+rt)^{k/t}-1} \quad \text{(See formula 20)}$$

The present value of such an annuity, were it to begin k years hence and continue for (a) years, equals

$$\frac{S\left[1-\frac{1}{(1+rt)^{a/t}}\right]}{(1+rt)^{k/t}-1} \quad \text{(See formula 20)}$$

The present value required is evidently the difference between the above expressions.

$$\text{Hence, } P = \frac{S\left[\frac{1}{(1+rt)^{a/t}} - \frac{1}{(1+rt)^{\frac{a+b}{t}}}\right]}{(1+rt)^{k/t}-1} \quad \ldots\ldots(30)$$

$$\text{If } b=\infty,\ P = \frac{S\left[\frac{1}{(1+rt)^{a/t}}\right]}{(1+rt)^{k/t}-1} = S\left[\frac{\frac{1}{(1+r)^{a}}}{r}\right]$$

$$(\text{if } k=t=1) \quad \ldots\ldots(31)$$

If the annuity is to begin (a) years hence and continue at the *beginning* of every interval of k years, etc., then it follows similarly that

$$P = \frac{S\left[(1+rt)^{\frac{k-a}{t}} - (1+rt)^{\frac{k-a-b}{t}}\right]}{(1+rt)^{k/t}-1} \quad \ldots\ldots(32)$$

$$\text{If } b=\infty,\ P = \frac{S\left[(1+rt)^{\frac{k-a}{t}}\right]}{(1+rt)^{k/t}-1} = S\left[\frac{(1+r)^{1-a}}{r}\right]$$

$$(\text{if } k=t=1) \quad \ldots\ldots(33)$$

To find the future value P^1, the value m years hence, of an annuity of S dollars payable at the *end* of of every k years for n years, interest compounded every t years.

P^1 is evidently equal to the amount of the annuity of S dollars for m years plus the present value of the annuity of S dollars for (n—m) years.

Hence, using formulas (11) and (20), we have

$$P^1 = S\left[\frac{(1+rt)^{m/t}-1}{(1+rt)^{k/t}-1}\right] + S\left[\frac{1-\frac{1}{(1+rt)^{\frac{n-m}{t}}}}{(1+rt)^{k/t}-1}\right]$$

$$= S\,\frac{\left[(1+rt)^{\frac{n-m}{t}} - 1\right]}{\left[(1+rt)^{k/t}-1\right]\ (1+rt)^{n/t}} \quad \ldots\ldots(34)$$

If k=1, t=1

$$P^1 = S\left[\frac{(1+r)^{2n-m} - 1}{r\,(1+r)^n}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (35)$$

If S is payable at the *beginning* of every period of k years, etc., then it follows similarly that

$$P^1 = S\left[\frac{(1+rt)^{\frac{m+k}{t}} + (1+rt)^{\frac{k-n-m}{t}}}{(1+rt)^{k/t} - 1}\right] \ldots (36)$$

If k=1, t=1:

$$P = \frac{S\left[(1+r)^{m+1} - (1+r)^{1-n-m}\right]}{r} \quad \ldots\ldots\ldots\ldots (37)$$

BONDS.

Bonds are written or printed obligations to pay a certain amount of money at a specified future time, together with the interest as at becomes due.

Let P=price of a bond in dollars.

n=time (in years) the bond has to run.

r=rate of interest on par value of bond.

V=face of the bond (V=P, if bought at par value).

s=current rate of interest, compounded every t years.

x=desired rate of interest on the investment.

$P\,(1+tx)^{n/t}$=value of the purchase money at the end of n years. [See formula (5)].

kVr=interest on the bond, received at the *end* of each interval of time k.

The total amount received from the bond in n years, if each installment of interest is immediately put at compound interest at 100s per cent=

$$kVr(1+ts)^{\frac{n-k}{t}} + kVr(1+ts)^{\frac{n-2k}{t}} \ldots + kVr + V =$$

$$V + kVr \times \frac{(1+ts)^{n/t} - 1}{(1+ts)^{k/t} - 1}$$

$$\text{Now, let } P(1+tx)^{n/t} = V + kVr \times \frac{(1+ts)^{n/t} - 1}{(1+ts)^{k/t} - 1}$$

$$\text{Hence, } (1+tx) = \left[\frac{V}{P} + \frac{kVr \times \left[(1+ts)^{n/t} - 1\right]}{P\left[(1+ts)^{k/t} - 1\right]}\right]^{1/n} \quad ..(38)$$

Example.

What interest will a purchaser receive on his investment if he buys at 120 a 6 per cent bond, with interest payable semi-annually, that has 25 years to run, money being worth 5 per cent.

$V=100$, $P=120$, $n=25$, $s=.05$, $t=1/2$, $k=1/2$.

$$(1+\tfrac{x}{2}) = \left[\frac{100}{200} + \frac{3\left[(1.025)^{50}-1\right]}{120 \times (.025)}\right]^{1/50} = 1.024 \text{ (Formula 38)}$$

$$\therefore x = .048 = 4.80\%.$$

FUTURE PROVISION FOR A BOND ISSUE.

Let it be desired to find what constant payment Q (including interest) must be made at the end of each period of k years in order to extinguish a principal A in n years, it being understood that each payment shall apply first to the interest due at the date of payment, and the remainder, after this is satisfied, be deducted from the principal before the interest for the next period is calculated.

It is evident that Q must be equivalent to the interest per period plus the sinking fund per period necessary to amount to the principal in n years. Hence, we have, using formula (12):

$$Q = \frac{A\left[(1+rt)^{k/t} - 1\right]}{(1+rt)^{n/t} - 1} + kAr \quad \ldots\ldots\ldots\ldots\ldots (39)$$

$$\text{If } k=1,\ t=1;\ Q = \frac{Ar}{(1+r)^{n} - 1} + Ar \quad \ldots\ldots\ldots\ldots\ldots (40)$$

If the payments are to be made at the *beginning* of each period of k years, then we have, using formula (15):

$$Q = \frac{A\left[(1+rt)^{k/t} - 1\right]}{(1+rt)^{\frac{n+k}{t}} - (1+rt)^{k/t}} + kAr \quad \ldots\ldots\ldots\ldots\ldots (41)$$

If $k=1$, $t=1$; $Q=\dfrac{Ar}{(1+r)^{n+1}-(1+r)}+\dfrac{Ar}{1+r}$ ..... (42)

To find the aggregate payment and the partial payments, if Y dollars and also the interest on the reduced principal are to be paid at the end of every period of k years, so that the whole debt will be cancelled in n years.

Let us assume $\dfrac{n}{k}$ = whole number.

Evidently, $Y=\dfrac{A}{(n/k)}=\dfrac{kA}{n}$

Total amount paid at end of first period of k years $=kAr+\dfrac{kA}{n}$

Amount at end 2nd period $=\left(\dfrac{A-kA}{n}\right)kr+\dfrac{kA}{n}$

Amount at end 3rd period $=\left(A-\dfrac{2kA}{n}\right)kr+\dfrac{kA}{n}$

Amount at end of $\left(\dfrac{n}{k}\right)^{th}$ period $=\left(A-\left(\dfrac{n}{k}-1\right)\left(\dfrac{kA}{kn}\right)\right)\times kr+\dfrac{A}{n}$

$$\text{Total}=kr\left[\frac{nA}{k}-\left[0+\frac{kA}{n}+\frac{2kA}{n}+\ldots\ldots\ldots\ldots+\left(\frac{n}{k}-1\right)\frac{kA}{n}\right]\right]+A$$

$$=Ar\left(\frac{n+k}{2}\right)+A \quad \ldots\ldots\ldots\

What will be the aggregate amount paid and how do the payments vary?

A=100,000, n=20, k=1, r=.04, Y=5000.

$$\text{Total} = 4000 \times \left(\frac{21}{2}\right) + 100{,}000 = \$142{,}000.$$

Difference between payments $= 4000 \times \frac{1}{20} = \$200$; that is, the annual payment would start at $9000 and decrease by $200 each succeeding year.

RELATIVE ECONOMY.

There are several methods of comparing the costs of articles of structures in order to decide which will be the most economical in the long run. All of these methods of comparison lead to the same relative result, as will be seen later. The following elements must be considered: (1) first cost; (2) life of article or structure; (3) cost of replacement or renewal; (4) rate of interest; (5) cost of maintenance; (6) salvage or scrap value of the article at the close of its period of usefulness.

CAPITALIZATION.

The capitalized cost of an article is that sum which is sufficien to pay the first cost and provide for future cost of maintenance and renewals forever.

Let C = first cost of article.

C^1 = cost of renewal.

M = cost of maintenance during each interval of k years.

n = life of article in years.

D = scrap value of article at end of n years.

r = rate of interest, compounded every t years.

X = required capitalized cost.

M^1 = the amount at compound interest necessary to produce at the end of every k years the cost of maintenance.

R = the amount which, when put at compound interest, will provide a sum at the expiration of the useful life of the article sufficient to renew it and also to leave a sum equal to the original amount (less the scrap value) for further future provision.

Then $X = C + M^1 + R$

Now, $M^1 = \dfrac{M}{(1+rt)^{k/t} - 1}$ (See formula (22); the present worth of a perpetual annuity.)

If R is placed at compound interest, as stated above, we must have

$$R\,(1+rt)^{n/t} = (C^1 - D) + R$$

$$\text{Whence } R = \frac{(C^1 - D)}{(1+rt)^{n/t} - 1}$$

Substituting these values of M^1 and R, we have the general formula for the capitalized sum:

$$X = C + \frac{M}{(1+rt)^{k/t} - 1} + \frac{(C^1 - D)}{(1+rt)^{n/t} - 1} \quad \ldots\ldots(44)$$

If k=1, t=1, and if $(C^1 - D) = C$, then

$$X = C + \frac{M}{r} + \frac{C}{(1+r)^n - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots(45)$$

In permanent structures the term R reduces to zero and we have the simple formula:

$$X = C + \frac{M}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots(46)$$

If only a portion of the structure is permanent, then the term C^1 represents the cost of renewal of the part which is not permanent.

Example.

The construction cost of certain waterworks of a city is estimated at $500,000, one-half being considered permanent, one-quarter to have a life of 20 years, and one-quarter a life of 50 years. Annual cost of operation and repairs equals $20,000. The rate of interest is assumed to be 4 per cent, compounded annually. What is the capitalized cost?

First cost=C=$500,000.

Repairs at end of 20 years=$125,000; renewal fund=

$$\frac{125{,}000}{(1.04)^{20} - 1} = \$104{,}945.00$$

Repairs at end of 50 years=$125,000; renewal fund=

$$\frac{125{,}000}{(1.04)^{50}-1} = 20{,}470.30$$

Maintenance fund= $\frac{20{,}000}{.04}$ = $500,000

Hence total capitalized cost=

$$500{,}000 + \frac{125{,}000}{(1.04)^{50}-1} + \frac{125{,}000}{(1.04)^{50}-1} + 500{,}000 =$$

$1,125,415.30.

COMPARISON OF COST ON BASIS OF ANNUAL EXPENSE.

The annual expense will consist of: (1) the annual interest on the first cost=I; (2) the amount that must be spent annually for maintenance=M; (3) the amount that must be set aside annually and placed at compound interest to provide for renewal at the expiration of the life of the article = $B = \frac{(C^1-D)r}{(1+r)^n-1}$ See formula (14).

Hence the total annual expense = I + M + B

$$= Cr + M + \frac{(C^1-D)r}{(1+r)^n-1} \quad \text{.....(47)}$$

It will be noticed that this is the same as Xr or the annual interest on the capitalized sum previously found.

The last term in formula (47) may be called the annual depreciation. The annual depreciation per unit of cost equals $\frac{r}{(1+r)^n-1}$

Example.

Two locations for a highway are under consideration. Route No. 1 is 10 miles long, will cost $2,000 per mile to construct it, and will require an outlay of $200 per year for maintenance. In addition to this, provision must be made for a $3,000 steel bridge, which probably must be renewed every 15 years (scrap value= $500, say). Route No. 2 is 11.2 miles long, will cost $1,600 per mile to build it and $325 per year for maintenance. A bridge will also be needed, which should be made of reinforced concrete, a permanent structure, costing $6,000.

With compound interest at 4%, which route will be the more economical?

Annual expense of route No. 1=

$$(20{,}000+3{,}000)\times.04+200+\frac{(3000-500)\times.04}{(1.04)^{15}-1}=\$1{,}244.85$$

Annual expense of route No. 2=

$(17{,}920+6{,}000)\times.04+325=\$1{,}281.80$

Hence route No. 1 would be slightly cheaper.

EXAMPLE.

Suppose a city with a population of 15,000 persons invests in a water supply system costing $600,000 and the annual operating expenses are as follows:

Fuel and oil	$20,000
Salaries	12,000
Supplies	3,000
	$35,000

The annual renewal and depreciation fund will be taken as 8% of the cost of the plant.

Bonds, redeemable in 20 years, are issued with interest at 5%. The increase of population is likely to double in 20 years, but it will be assumed that future needs can be provided for by additional pumps and that their cost will have the same relation to the increase in earnings as the original cost has to the present income, hence provision for future enlargement of plant will not be considered in the problem.

The water consumption will amount to 100 gallons per person per day. It is required to determine the selling price of 1,000 cubic feet of water and the annual cost per capita.

The annual revenue necessary embraces the following:

Sinking fund to pay the bonds 20 years hence $=\frac{600{,}000\times.05}{(1.05)^{20}-1}$	$18,145
Interest on bonds=.05×600,000	30,000
Operating expenses	35,000
Renewal and depreciation fund = .08×600,000	48,000
	$131,145

$$\text{Annual cost per capita} = \frac{131{,}145}{15{,}000} = \$8.76.$$

$$\text{Water consumption per year} = \frac{15{,}000 \times 100 \times 365}{7.48} = 73{,}200{,}000 \text{ cubic feet.}$$

$$\text{Cost per 1,000 cubic feet} = \frac{131{,}145}{73{,}200} = \$1.79.$$

COMPARISON OF COST OF TWO ARTICLES ON BASIS OF EQUIVALENT CAPITALIZED COST.

Let X^1 = capitalized cost of one article.
X = " " " other "

Assume the cost of renewal equal to the first cost, then, using formula (45):

$$X = C + \frac{C}{(1+r)^n - 1} + \frac{M}{r} = \frac{C\,(1+r)^n}{(1+r)^n - 1} + \frac{M}{r}$$

Similarly, $X^1 = \frac{C^1\,(1+r)^{n'}}{(1+r)^{n'} - 1} + \frac{M^1}{r}$ where C is the cost of one article of life of n years and C^1 is the cost of the other article with life of n' years.

Letting $X = X^1$ and solving, we have:

$$C = \left[\frac{C^1\,(1+r)^{n'}}{(1+r)^{n'} - 1} \times \frac{(1+r)^n - 1}{(1+r)^n}\right] + \left[\frac{M^1 - M}{r} \times \frac{(1+r)^n - 1}{(1+r)^n}\right] \quad \text{.....(48)}$$

Neglecting the cost of maintenance, that is, letting $M^1 - M = 0$, we have

$$C = \left[\frac{C^1(1+r)^{n'}}{(1+r)^{n'} - 1} \times \frac{(1+r)^n - 1}{(1+r)^n}\right] \quad \text{.....(49)}$$

Example

How much may be paid for a crosstie lasting 16 years to show the same merit as a tie lasting 7 years and costing 55 cents, interest at 5%?

$n=16$, $n'=7$, $C'=0.55$.

Using formula (49),

$$C = 0.55 \times \left[\frac{(1.05)^7}{(1.05)^7-1} \times \frac{(1.05)^{16}-1}{(1.05)^{16}}\right] = \$1.03.$$

This shows that a railway company could afford to spend $0.48 per tie for treatment with some preservative oil in order to make the ties last 16 years instead of 7 years.